# Hartree-Fock exchange and hybrid functionals in ONETEP

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ONETEP masterclass 2019

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# Preamble

Slides will soon be available online at
http://www.onetep.org/Main/Workshops

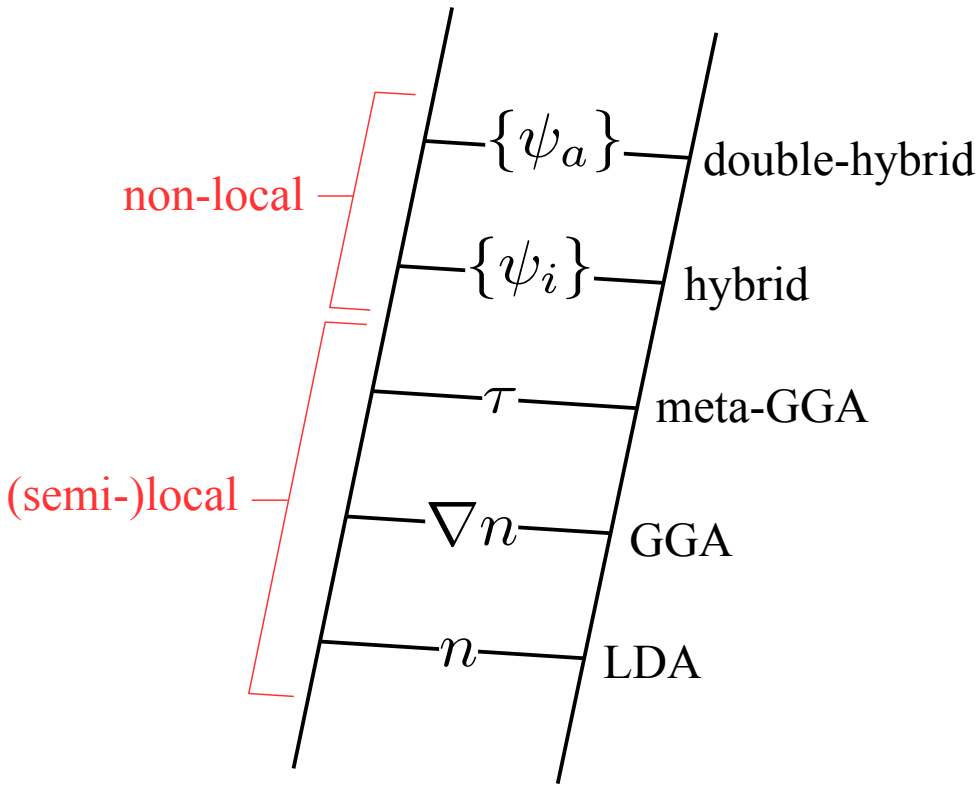
See slides online for bibliography

# Hartree-Fock exchange and hybrid functionals

- Hybrid functionals depend on $\{\psi_i\}$ via $E_{\mathrm{HFX}}$
- HFX corrects self-interaction error in Coulomb energy
- The most accurate XC functionals include HFX [1]

$$E_{\mathrm{HFX}} = -\sum_{i=1,j=1}^{N_{\mathrm{MO}}} z_i z_j \, (\psi_i \psi_j | \psi_j \psi_i)$$

$$\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_j(\mathbf{r}) \psi_i(\mathbf{r}')$$




Ascending towards the "heaven of chemical accuracy" [2, 3]. . .

# Global hybrid functionals

Combine (semi-)local XC and HFX in a constant ratio over all space

e.g. Becke 3-parameter hybrids [4, 5], such as B3LYP [6]

$$E_{\mathrm{xc}}^{\mathrm{B3hyb}} = E_{\mathrm{xc}}^{\mathrm{LDA}} + a_0 \left( E_{\mathrm{x}}^{\mathrm{HFX}} - E_{\mathrm{x}}^{\mathrm{LDA}} \right) + a_{\mathrm{x}} \Delta E_{\mathrm{x}}^{\mathrm{B88}} + a_{\mathrm{c}} \Delta E_{\mathrm{c}}^{\mathrm{GGA}}$$

Range-separated hybrids are under development in ONETEP

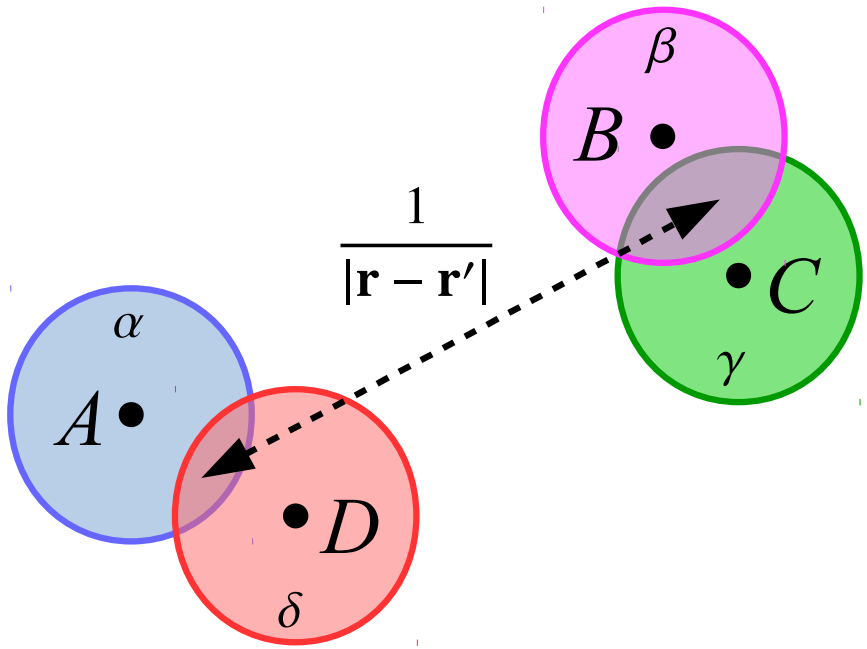
# Linear-scaling Hartree-Fock exchange (LS-HFX)

HFX is challenging for $\mathcal{O}(N)$ DFT because ERIs are non-local

- (Semi-)local XC does not require **E**lectron **R**epulsion **I**ntegrals
- BUT ERIs are needed to evaluate HFX for hybrids. . .

$$(\varphi_\alpha \varphi_\delta | \varphi_\beta \varphi_\gamma)$$

$$\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \varphi^*_\alpha(\mathbf{r})\varphi_\delta(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\varphi^*_\beta(\mathbf{r}')\varphi_\gamma(\mathbf{r}')$$

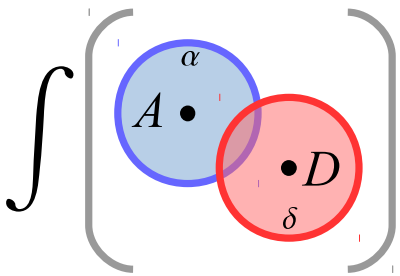


# LS-HFX with NGWFs

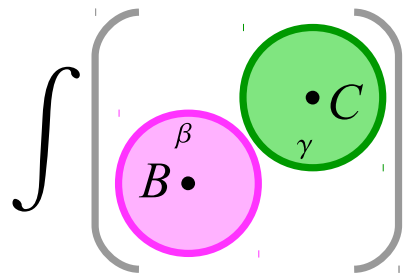
The strictly localized NGWF basis presents unique challenges

$$E_{\mathrm{x}}^{\mathrm{HFX}} = -K^{\beta\alpha}(\varphi_\alpha\varphi_\delta|\varphi_\beta\varphi_\gamma)K^{\delta\gamma}$$
$$= -K^{\beta\alpha}X_{\alpha\beta}$$

- NGWFs produce sparse matrices & simplified integrals




$\mathbf{dr} \neq 0$




$\mathbf{dr} = 0$

- BUT cannot use conventional ERI evaluation methods
- Straightforward HFX evaluation (via FFTs) is impractical [7, 8]

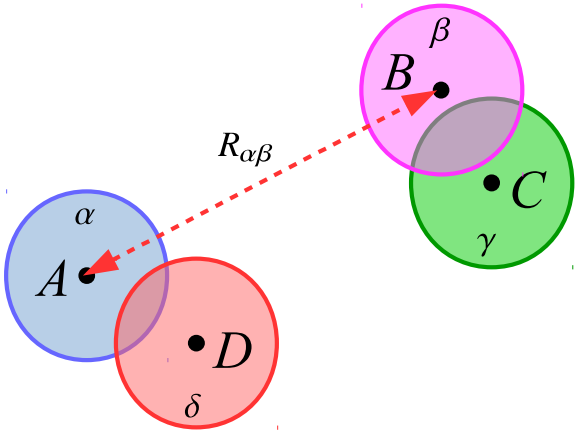
An alternative scheme is necessary!

# LS-HFX with NGWFs

## Defining features of the scheme [7]

$$X_{\alpha\beta} = (\varphi_\alpha \varphi_\delta | f_p) V^{pq} (f_q | \varphi_\beta \varphi_\gamma) K^{\delta\gamma}$$

- Spherical wave (SW) [9] resolution-of-the-identity (RI)
- Distance-based exchange cutoff



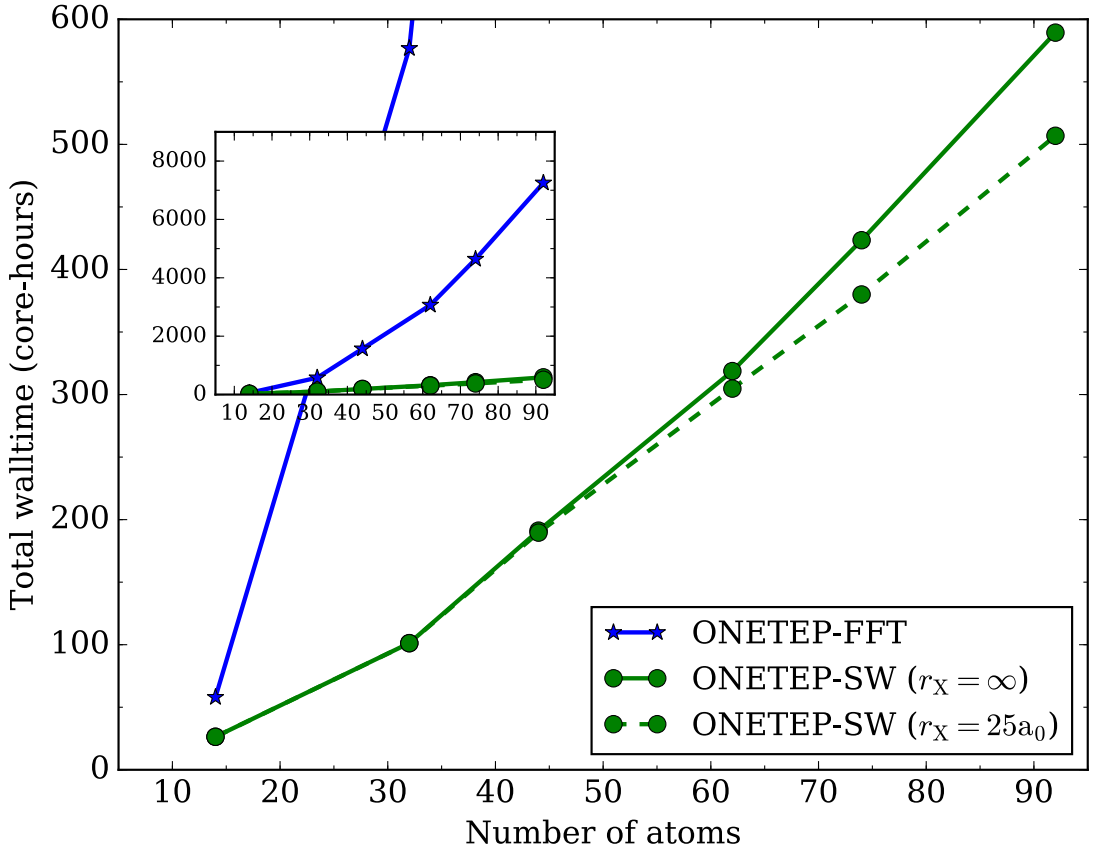

$$R_{\alpha\beta} > r_X \implies X_{\alpha\beta} = 0$$

## Expand NGWF products in SWs

- Strictly localized in a sphere
- Analytic Coulomb potentials
- “2-centre” fitting scheme

$$f_p(\mathbf{r}) = \begin{cases} j_{l_p}(q_p r) Z_{l_p m_p}(\hat{\mathbf{r}}) & r < a \\ 0 & r \geq a \end{cases}$$

# Demonstration of $\mathcal{O}(N)$ scaling HFX




Polyethylene chains

$H-(CH_2)_n-H$

Cost in core-hours

$N_{CPU} \times$ walltime

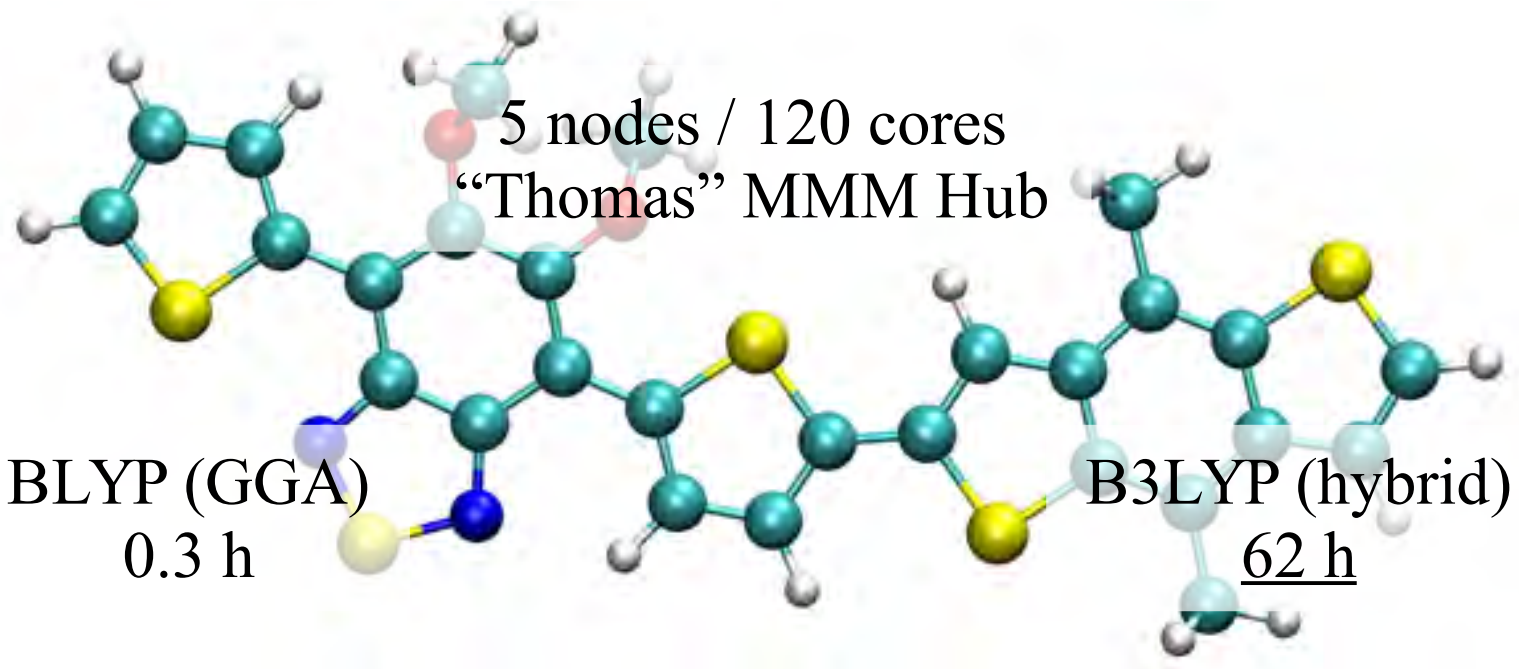
Data from 2013 [7]

Some improvements since

Linear-scaling is achieved, but with a large prefactor. . .

# A few years later. . .

Single-point DFT energy with and without HFX




57 atom monomer from organic photovoltaic polymer

Before recent developments to significantly improve performance. . .

# Accelerated SW Coulomb metric matrix evaluation

**V** is central to the SW resolution-of-the-identity

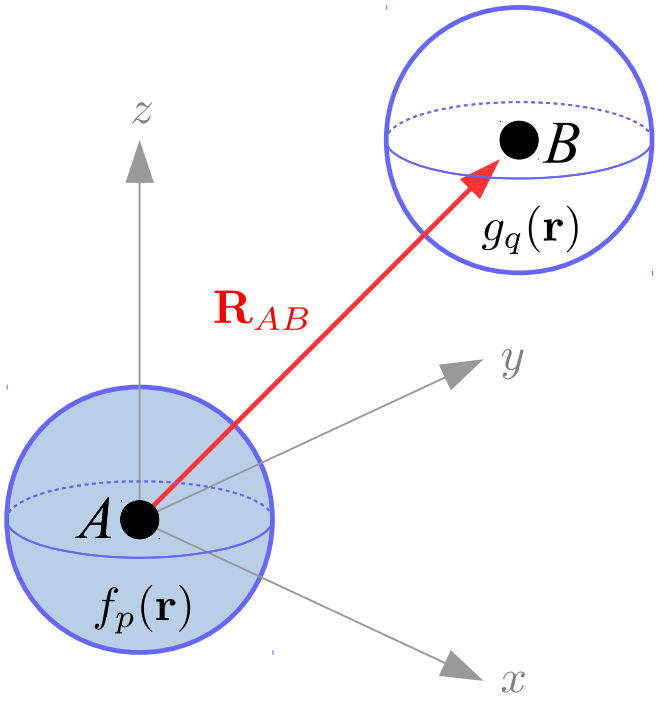
$$V_{Ap,Bq} = \int \mathrm{d}\mathbf{r}\, f_p(\mathbf{r}_A) g_q(\mathbf{r}_B) \qquad g_q(\mathbf{r}) = \int \mathrm{d}\mathbf{r}' \frac{f_q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- Integrand is highly oscillatory
- Closed-form solutions only for same-centre case ($A = B$)
- Must resort to numerical integration for "off-site" case $A \neq B$

Main developer: James Womack

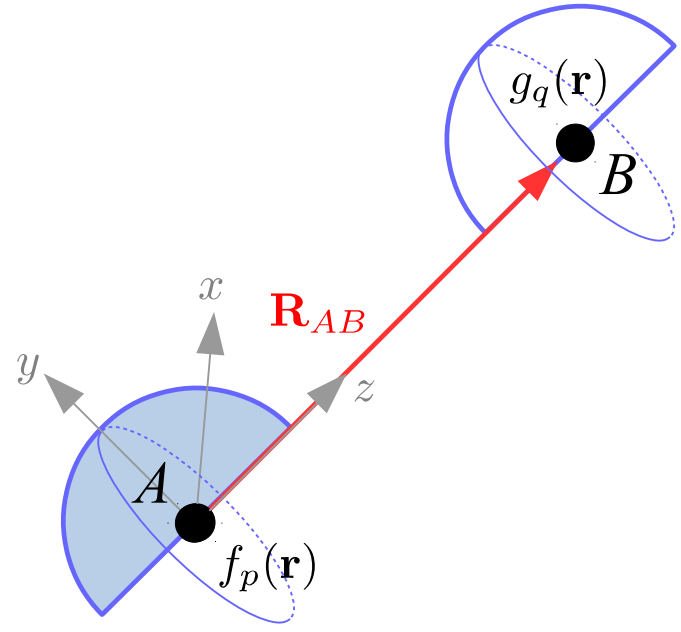
# Accelerated SW Coulomb metric matrix evaluation

**Old:** 3Dc



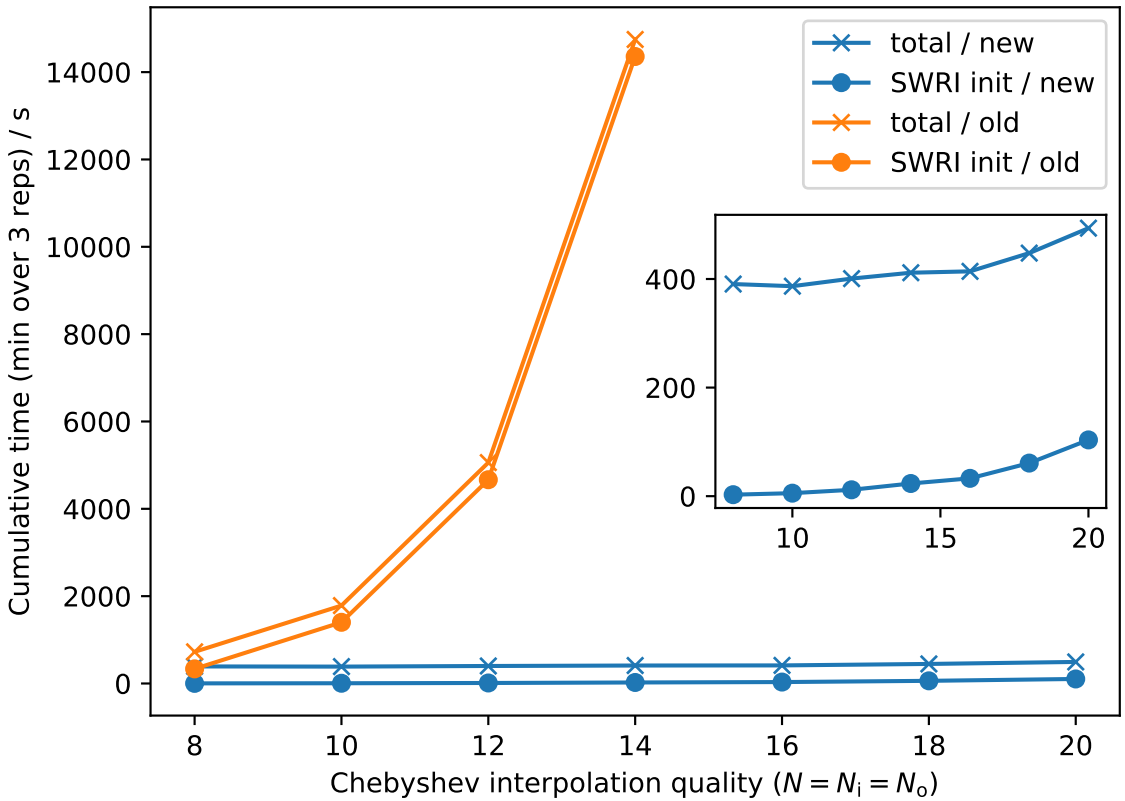

- Computationally expensive
- Memory: $O(N^3_{\text{node}})$
- Bottleneck for HFX

**New:** 2Dn-1Da




- Significantly reduced cost
- Memory: $O(N^2_{\text{node}})$
- Small fraction of HFX cost

# Accelerated SW Coulomb metric matrix evaluation




Myoglobin model
27 atoms

Single inner loop
**V** evaluation
HFX energy

Iridis 5
1 node ($2 \times 20$ cores)
10 MPI / 4 OMP

New scheme also makes much larger systems accessible. . .
13696 atoms, 1000 cores on Iridis 5: **V** evaluation took 30 min

# Improved parallelisation

**Old:** poor scaling for > 50 CPUs

- Convoy effects from mixing comms and compute
- Usual atom-to-MPI distribution unsuited for HFX
- OpenMP sections too finely grained / low-level

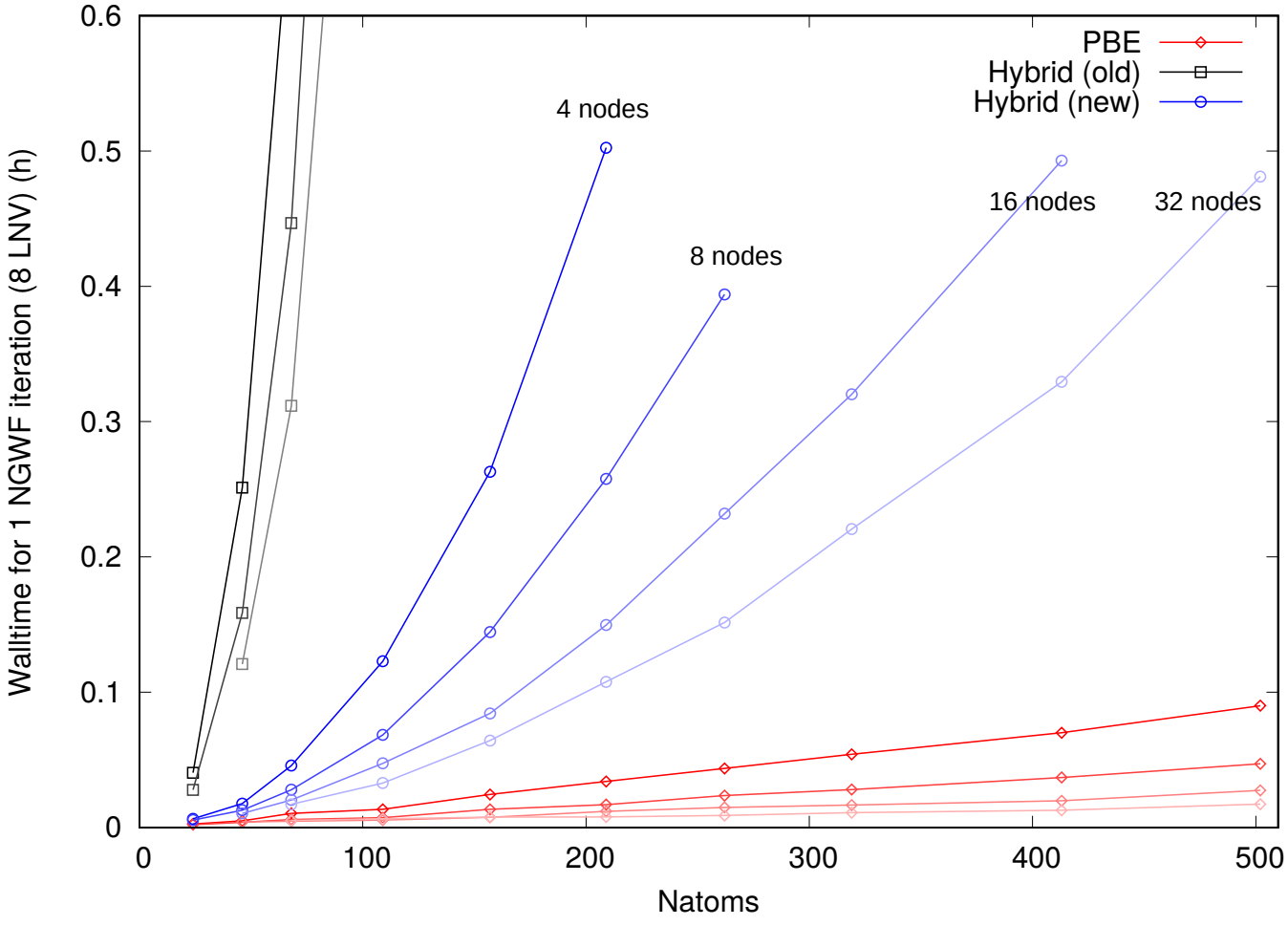
Main developer: Jacek Dziedzic

**New:** scales to 1000s of cores

- "Dry-run" to perform comms in advance
- Atom-pair-to-MPI distribution for HFX
- OpenMP sections moved to higher level
- Aggressive caching in thread-shared memory
- *Cleverness*: intelligently caching most used quantities

# Improved parallelisation

## Protein “scoops” on Iridis 5 (April 2019)




Much larger systems are now practially accessible

# Setting up a calculation

## Key settings when using a hybrid functional

- Spherical wave resolution-of-the-identity (SWRI) setup
- Hartree-Fock exchange (HFX) setup
- Selecting an XC functional

```
%block swri
  for_hfx 3 10 V 12 12 WE2
%endblock swri

%block species_swri-for_hfx
O
C
H
%endblock species_swri-for_hfx

hfx_use_ri              : for_hfx
hfx_max_l               : 3
hfx_max_q               : 10
hfx_cutoff              : 20 bohr
hfx_metric              : ELECTROSTATIC

cutoff_energy           : 800 eV
xc_functional           : B3LYP
```

# SWRI setup

$$X_{\alpha\beta} = (\varphi_\alpha \varphi_\delta | f_p) V^{pq} (f_q | \varphi_\beta \varphi_\gamma) K^{\delta\gamma}$$

$$f_p(\mathbf{r}) = \begin{cases} j_{l_p}(q_p r) Z_{l_p m_p}(\hat{\mathbf{r}}) & r < a \\ 0 & r \geq a \end{cases}$$

```
%block swri
  myname lmax qmax metric Ni No flags
%endblock swri

%block species_swri-myname
atom-label-1
atom-label-2
...
%endblock species_swri-myname
```

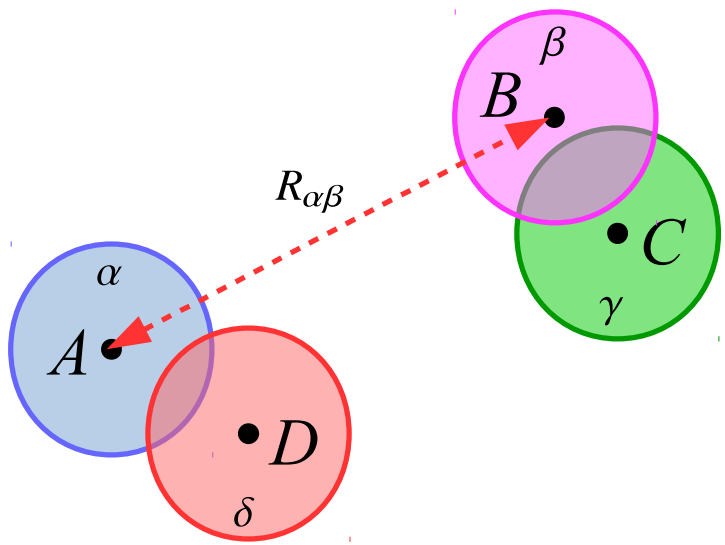
| Setting | Description | Recommendation |
|---|---|---|
| *myname* | label for SW basis/metric | short string |
| $l_{\max}$ | maximum angular momentum in SW basis | ≥3 |
| $q_{\max}$ | number of spherical Bessels per $l$ | ≥10 |
| *metric* | metric type | V (electrostatic) |
| $N_i$ | numerical integration intervals | ≥12 |
| $N_o$ | numerical integration polynomial order | ≥12 |
| *flags* | metric matrix evaluation control | see documentation |
| *atom-label-X* | atoms to include in SWRI | all atom labels |

# HFX setup

| Keyword and value | Description | Recommended value |
|---|---|---|
| `hfx_use_ri` *myname* | label for SW basis/metric to use | short string |
| `hfx_max_l` $l_{\max}$ | max. ang. mom. in SW basis | ≥`3` |
| `hfx_max_q` $q_{\max}$ | number of spherical Bessels per $l$ | ≥`10` |
| `hfx_cutoff` $r_X$ *[unit]* | cutoff for exchange interactions | ≥`20 bohr` |
| `hfx_metric` *metricname* | metric type (name) | `ELECTROSTATIC` |

$$E_X^{\mathrm{HFX}} = -K^{\beta\alpha}(\varphi_\alpha\varphi_\delta|\varphi_\beta\varphi_\gamma)K^{\delta\gamma}$$
$$= -K^{\beta\alpha}X_{\alpha\beta}$$

$$R_{\alpha\beta} > r_X \implies X_{\alpha\beta} = 0$$



# XC functional selection

`xc_functional` *`funcname`*

Available hybrid functionals:
`B1LYP`, `B1PW91`, `PBE0`, `B3LYP`, `B3PW91`, `X3LYP`

For 100% Hartree-Fock exchange, use `HF`

# Understanding the output

## A successful calculation

- Similar to local XC calculation with `normal` output detail
- Local XC ( $E_{xc}^{loc}$ ) and HFX ( $E_{x}^{HF}$ ) energies reported

```
---------------- ENERGY COMPONENTS (Eh) ----------------
| Kinetic                       :       27.35982130694516 |
| Pseudopotential (local)       :     -126.10605114635337 |
| Pseudo (non-coul chg cor)     :        0.00000000000000
| Pseudopotential (non-local):         5.13945962391166 |
| Hartree                       :       48.59030602370854 |
| Exchange-correlation          :       -7.97965813472141 |
| Hartree-Fock exchange         :       -1.78484725447100 |
| Ewald                         :       14.80743332976961 |
| Total                         :      -39.97353625121082 |
--------------------------------------------------------------
Integrated density              :       19.99999999999997
```

# Understanding the output

SWRI details: metric matrix method, metric type, memory usage, progress evaluating metric matrix

```
SWRI: Initialising module (stage 1)...
SWRI: [hfx] Initialising (stage 1)...
SWRI: [hfx] - Using user-selected metric matrix evaluation scheme (2D numerical-1D analytic).
SWRI: [hfx] - Initialising Bessels (l_max=3)... done.
SWRI: [hfx] - SW batch size (tile width) set to 160.
SWRI: [hfx] - Initialising persistent cache structures... done.
SWRI: [hfx] - Initialising metric matrix... done.
SWRI: [hfx] Done.
SWRI: Stage 1 completed.
Sparse matrix initialisation ... done

SWRI: Initializing module (stage 2)...
SWRI: [hfx] Initialising (stage 2)...
SWRI: [hfx] - NL: Populating neighbour list: SWRI_S_ATOMS... done.
SWRI: [hfx] - Generating and communicating atomblock list.
SWRI: [hfx]   0 atomblocks read from disk.
SWRI: [hfx]   21 atomblocks to process.
SWRI: [hfx]   Sorting atomblocks according to proximitiy to (0.000000,    0.000000,
    0.000000).
SWRI: [hfx] - Calculating on-site elements of the metric matrix V... done.
SWRI: [hfx] - Calculating off-site elements of the metric matrix V.
```

# Understanding the output

SWRI details: metric matrix method, metric type, memory usage, progress evaluating metric

```
 +-----------------------------------------------------+
 |  Spherical wave res. of identity Chebyshev engine   |
 |  Estimated memory requirement per MPI rank          |
 +-----------------------------------------------------+
 |  workspace atomblock                 :  200.00 kB   |
 |  vtile                               :  200.00 kB   |
 |  recvtile                            :  200.00 kB   |
 |  workers_done                        :   24.00  B   |
 |  atomblocklist                       :  420.00  B   |
 |  tilelist (root only)                :  252.00  B   |
 |  tile hash table (upper bound)       :    1.17 MB   |
 |  nodes_template                      :  162.00 kB   |
 |  swop_values                         :  648.00 kB   |
 |  swy_values                          :  648.00 kB   |
 |  swhome_all_coeffs                   :   25.31 MB   |
 |  swpot_batch_coeffs                  :   25.31 MB   |
 |  all_atomblocks (indices)            :  252.00  B   |
 |  my_atomblocks (indices)             :  252.00  B   |
 |  num_q_per_l                         :   48.00  B   |
 |  atomblock rotation matrix           :  200.00 kB   |
 +-----------------------------------------------------+
 |  Estimated peak total per MPI rank   :   54.00 MB   |
 +-----------------------------------------------------+
```

```
SWRI: [hfx]   21 tiles to process (21 atomblocks x 1 batches)
SWRI: [hfx]   Tiles completed:       0, left:      15, in progress:       6.
SWRI: [hfx]   Tiles completed:       6, left:       9, in progress:       6.
SWRI: [hfx]   Tiles completed:      12, left:       3, in progress:       6.
SWRI: [hfx]   Tiles completed:      18, left:       0, in progress:       3.
SWRI: [hfx] - Filling the remainder by symmetry.
SWRI: [hfx] - Writing for_hfx.vmatrix to file "h_bond_B3LYP_2Dn-1Da_modified.for_hfx.vmatrix"...done
SWRI: Done.
SWX: Initialising module...
done.
```

# Tips for maximising performance

## HFX is. . .

- Much more expensive than local XC
- Very memory-hungry (RAM)

## Improve performance by. . .

- Always using the new metric matrix (2Dn-1Da) scheme (default)
- Choosing a sensible exchange cutoff $r_X$
- Increasing the $\frac{N_{OMP}}{N_{MPI}}$ ratio (more RAM per MPI process)
- Increasing per process cache limits to fully utilise node memory

```
cache_limit_for_swops     cache_limit_for_expansions
cache_limit_for_ps        cache_limit_for_ngwfs
cache_limit_for_dknblks   cache_limit_for_coeffs
```

These apply to version of HFX in v5.2 and earlier

# Further information

For practical usage, see online documentation

"Spherical-wave resolution of identity (SWRI), Distributed Multipole Analysis (DMA), and Hartree-Fock exchange (HFx)"

For theory and technical details, see Ref. 7

J. Dziedzic, Q. Hill, and C.-K. Skylaris, J. Chem. Phys. **139**, 214103 (2013)

Publications on recent developments coming soon. . .

# Acknowledgements


## Funding and compute resources

- EPSRC-funded CCP9 flagship (EP/P02209X/1)
- UK MMM Hub "Thomas" (EP/P020194/1)
- IRIDIS HPC Facility (Southampton)


## CCP9 flagship collaborators

- Nick Hine (Warwick, PI)
- Peter Haynes (Imperial, Co-I)
- Arash Mostofi (Imperial, Co-I)
- Chris-Kriton Skylaris (Southampton, Co-I)
- Jacek Dziedzic (Southampton/Gdańsk, RCo-I)
- Jolyon Aarons (Warwick, PDRA)
- Joseph Prentice (Imperial, PDRA)

EPSRC
Engineering and Physical Sciences Research Council

UNIVERSITY OF Southampton

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Imperial College London

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